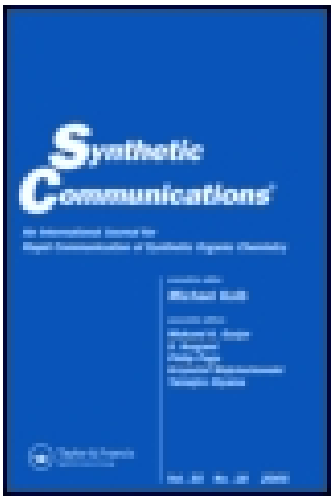

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Reductive Cleavage of Se-Se and Te-Te Bond by Samarium Diiodide: Synthesis of Selenoesters, Telluroesters, Unsymmetrical Alkylphenyl Selenides and Tellurides

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REDUCTIVE CLEAVAGE OF Se-Se AND Te-Te BOND BY SAMARIUM DIIODIDE: SYNTHESIS OF SELENOESTERS, TELLUROESTERS, UNSYMMETRICAL ALKYLPHENYL SELENIDES AND TELLURIDES

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ABSTRACT: The reduction of diaryl diselenides and ditelluides by samarium diiodide led to samarium arylselenolates and samarium aryltellurolates respectively ($ArSeSmI_2$ and $ArTeSmI_2$). These species reacted smoothly with acyl halides and alkyl halides to give selenoesters and alkylselenides or telluroesters and alkyltellurides in good yields under mild and neutral condition.

Organoselenium and organotellurium compounds have attracted considerable interest as reagents and intermedieates in organic synthesis recently[1]. A convenient and general method to introduce a selenium or tellutium moiety into organic molecules is the

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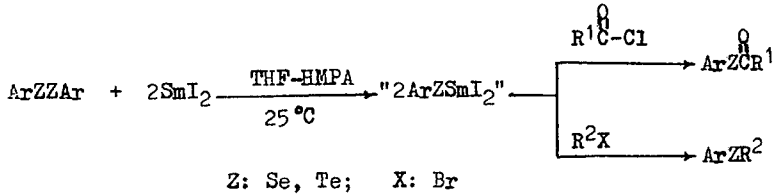
reaction of a metal selenoate or tellurolate with approriate electrophiles. As a powerful and versatile one electron transfer reducing and coupling reagent, SmI_2 has wildly been applied in organic synthesis[2]. Our previous work on some deoxygenation with SmI_2 has led us to investigate on the reductive cleavage of Se-Se and Te-Te bond by SmI_2. Here we wish to report a convenient synthetic method of selenoesters, telluroesters, unsymmetric alkylphenyl selenides[4] and tellurides by the reaction of samarium arylselenolates and samarium aryltellurolates with acyl halides and alkyl halides respectively.

We found that under mild conditions, samarium arylselenolates or samarium aryltellurolates, easily prepared in situ from the cleavage of thr corresponding diaryl diselenides or ditellurides with SmI_2 in THF-HMPA system, reacted smoothly with acyl halides to afford the desired selenoesters or telluroesters and unsymmetric alkylphenyl selenides or tellurides respectively in good yields. The results were summarized in Table 1. This method for synthesis of selenoesters and telluroesters appears to be among the practical methods in terms of good yield, mild and neutral conditions in an aprotic solvent.



Experimental

Instruments and materials.

^1H NMR spectra were recorded on FX-90Q spectrometer, using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 spectrophotometer. Melting points were uncorrected. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Commercial HMPA was dried over calcium hydride, distilled in vacuo and stored over 4A molecular sieves, Diaryl diselenide and ditelluride were prepared by the reaction of phenylmagnesium bromide with selenium and tellurium[5-6]. Samarium diiodide (SmI_2) was prepared by the reaction of samarium powder with iodine in freshly distilled THF[7].

A representative procedure for the synthesis of selenoester or telluroester:

The deep blue solution of SmI_2 (2.2 mmol) in THF (22 ml) was added with HMPA (2 ml) and the solution became deep purple. To the THF-HMPA solution of SmI_2 was then added diphenyl diselenide (0.34g, 1 mmol) or ditelluride (0.42g, 1 mmol) in one portion at room temperature under nitrogen atmosphere. The mixture was stirred for 1 h. To the mixture was added successively acyl halide (2.5 mmol), then stirred at room temperature for 2 h. The reaction mixture was diluted with Et_2O(50 ml), then washed three times with brine (30 ml x 3). The organic layer was dried over $MgSO_4$, and evaporated to give a yellow oil. The oil was then subjected to preparative TLC on silica gel (n-hexane as eluent) provided the desired selenoester or telluroester.

Table 1. Physical constants and spectra data of the products

No.	Product	m.p.(℃) (Lit)	Yield (%)	^{1}H NMR (ppm)	IR (cm^{-1})
1	$PhSeC(=O)Ph$	39-40 (40)	81	7.82(m,2H), 7.40(m,8H)	3050, 1690, 1610, 1100
2	$PhSeC(=O)CH_3$	oil	75	7.40(m,5H), 2.39(s,3H)	3050, 1740, 1600, 1105
3	$PhTeC(=O)Ph$	70-71 (70-72)	77	7.80(m,2H), 7.45(m,8H)	3050, 1675, 1595, 1100
4	$p\text{-}CH_3PhTeC(=O)Ph$	65-68 (66-67)	72	7.20-7.75(m,9H), 2.40(s,3H)	3055, 1680, 1650, 1110
5	$PhSeCH(CH_3)_2$	oil	78	7.68-7.34(m,2H), 7.30-7.08(m,3H), 3.08-3.01(m,1H), 1.38(d,6H)	1148, 1250, 1065
6	$PhSeCH_2C(=O)Ph$	oil	68	7.73(m,2H) 7.50-7.05(m,8H) 4.20(s,2H)	3050, 1685, 1600, 1590
7	$PhTe(CH_2)_3CH_3$	oil	71	8.07-7.58(m,2H), 7.30-7.10(m,3H), 2.83 (m,2H), 2.00-1.20(m,4H), 0.90(m,3H)	1448, 1255, 1090
8	$PhTeCH(CH_3)_2$	oil	73	7.60-7.40(m,2H), 7.30-7.10(m,3H), 3.50-3.10(m,1H), 1.30(d,6H)	1140, 1250, 1070

A representative procedure for the synthesis of unsymmetrical alkylaryl selenide or telluride:

To the THF-HMPA (22 ml--2 ml) solution of SmI_2 (2.2 mmol), prepared as described above, was added a mixture of diaryl diselenide (0.34g, 1 mmol) or ditelluride (0.42g, 1 mmol) and organic halide (2 mmol) in THF (5 ml) at room temperature. The solution was stirred under reflux for 3 h, and the same workup procedure provided the desired alkylaryl selenide or telluride.

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